Supplementary Information

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References

1 Appendix A: Self-Reaction Scheme

Below is the generally accepted mechanism¹ for the formation of the peroxide accretion product and other self-reaction products.



Figure S1: Peroxy radical self-reaction mechanism, based on the currently proposed mechanism 1 for these reactions.

2 Appendix B: Experimental Conditions

Experiment No.	Exp. Date	$[Ethene]_0$	$[\mathrm{H}_2\mathrm{O}_2]_0$	$[Methanol]_0$	$[2,3-butanediol]_0$
1	1/19/2022	3057	1416	579	0
2	1/21/2022	2923	2057	40000	0
3	1/24/2022	3033	270	1.8	0
4	1/25/2022	3126	686	0	0
5	1/26/2022	3735	655	0	0
6	1/27/2022	3771	1646	1450	0
7	2/8/2022	3045	1377	3500	0
8	2/16/2022	3603	1920	110650	0
9	2/22/2022	3102	1963	4810	0
10	2/28/2022	3077	1944	8961	0
11	3/1/2022	3000	1520	13780	0
12	3/14/2022	3075	1645	78108	0
13	3/16/2022	3073	1919	120200	0
14	3/21/2022	2769	497	0	0
15	3/22/2022	3173	1974	97300	0
16	3/29/2022	3076	2222	88239	0
17	3/29/2022	3074	1322	104.3	0
18	5/17/2022	1827	753	0	6.0
19	6/1/2022	428	966	0	537
20	6/2/2022	479	486	0	631

Table S1: Experimental Conditions. All concentrations are in ppbv. All experiments have lights on time of 2 minutes.

3 Appendix C: Additional Experimental Results

Photolysis Experiments and Post-Photolysis Dark Decay Rate Frequency. The measured mean photolysis frequency of H_2O_2 in our chamber over a 120 s period of lamp illumination was determined by measuring the 'OH production via the decay of 2,3 butanediol. We measured the photolysis frequency of glycolaldehyde by injecting gas-phase glycolaldehyde into the atmospheric chamber along with sufficient methanol to remove any 'OH produced. The gas-phase glycolaldehyde monomer was prepared by heating solid glycolaldehyde dimer (Sigma Aldrich) in a water bath maintained at 85°C. Upon heating, the glycolaldehyde dimer decomposed to the monomer and was moved and collected in a 200-L Teflon bag using a stream of N₂ gas. A 500-mL glass bulb was filled from the 200-L bag and transfered to the 600-L Teflon chamber bag. We measured the decay rate of the glycolaldehyde irradiated with 8 254 nm UV lamps for approximately 15 minutes (Figure S2).

ROOH and ROOR mean photolysis frequencies are an average of two 300 s photolysis experiments, performed as described in the main body of the paper. After the lights were turned off, dark decay of both the ROOR and ROOH were observed, in addition to a small rapid increase in the concentration after lights were turned off due to mixing in the bag. The post-photolysis loss was quantified by fitting the decay in each compound after the lights were turned off. These rates were found to be $5.5(\pm 0.8) \times 10^{-5} \text{ s}^{-1}$ for the ROOR and $3.4(\pm 0.7) \times 10^{-5} \text{ s}^{-1}$ for the ROOH. To account for these effects in the calculation of the photolysis frequencies, we corrected the signals of these compounds throughout the experiment with the measured wall loss. The difference between the final and the initial concentration of each compound was then used to calculate the photolysis frequencies. The ROOR and ROOH photolysis data are given in Table S3. Note that these photolysis frequencies are uncertain, and should be considered to be an upper limit to the true photolysis frequencies of these compounds, since there may be additional losses during these photolysis experiments.

The mean photolysis frequencies listed in the main body of the paper for 120 s experiments

are calculated using measurements of the time dependence of the cosine-corrected irradiance measurements (Ocean Optics spectrometer integrated between 224 and 284 nm). The light emission increases over time as the bulbs warm up. Compared to the first 120s, the mean irradiance is 20% and 34% higher for 300 and 900 s experiments, respectively. Table S2 gives the measured photolysis frequencies and the time over which they were measured, along with the comparison between the mean irradiance over the measured time and the experiment time of 120s.

Table S2: Photolysis Reactions. $R = HOCH_2CH_2$. Photolysis time gives the time over which the photolysis frequency was measured. I_t is the mean irradiance of the lights over t seconds, where t is the photolysis time, and I_{120} is the mean irradiance of the lights over 120s.

Assumed Reaction	Mean Photolysis frequency (s^{-1})	Photolysis Time (s)	$\frac{I_t}{I_{120}}$
	1 0 ()		
$\rm H_2O_2 \rightarrow `OH + `OH$	3.0×10^{-4}	120	1.0
$\mathrm{ROOH} \rightarrow \mathrm{RO^{*}} + \mathrm{^{*}OH}$	$< 6.3 \times 10^{-4}$	300	1.2
$ROOR \rightarrow RO' + RO'$	$<7.3\times10^{-4}$	300	1.2
$\rm HOCH_2CHO \rightarrow \rm HO\dot{C}H_2 + \rm HCO$	2.3×10^{-4}	900	1.35

Table S3: ROOR and ROOH Photolysis Results. All concentrations are reported in ppbv.

	Initial [ROOH]	Final [ROOH]	Initial [ROOR]	Final [ROOR]
Experiment 1	5.1	4.2	2.6	1.9
Experiment 2	10.4	8.2	6.3	4.8



Figure S2: Decay of glycolaldehyde during photolysis experiment.

Experiments with Steel and Quartz Tubing. The hydroxyhydroperoxide and the accretion product are lost rapidly on quartz and stainless steel. We performed two ethene oxidation experiments in the high RO_2 limit and replaced the Teflon tubing between the bag and the CIMS instrument with approximately 60 cm of 1/4 inch O.D. quartz or steel tubing with a residence time of < 3 s. The results of these experiments are shown in Figure S3. There is a large loss of the signal at m/z 207 and m/z 163 after the insertion of these tubing materials.



Figure S3: ROOR concentration before and after insertion of quartz and steel tubing. When quartz tubing was initially inserted, the flow through tubing was approximately 1 L/min, resulting in a residence time of approximately 0.3 s. During the period of slow flow during quartz experiment and in the steel experiment, the flow through the tubing was approximately 200 mL/min, resulting in a residence time of approximately 1.4 s.

Glycolaldehyde Production. More glycolaldehyde than ethylene glycol is produced in the peroxy radical self-reaction, and this excess increases with $[O_2]$. We performed a few experiments in the 'high RO₂' limit in which we varied the mixing ratio of O₂ and quantified the yields of glycolaldehyde and ethylene glycol. At approximately 1% O₂, we find the ratio of glycolaldehyde to ethylene glycol formation to be 1.3 ± 0.3 , including uncertainties in sensitivities. To compare the results of our experiments probing the oxygen sensitivity of glycolaldehyde formation to those of Orlando et al,² we compare the derived value of $\frac{k_{7b}[O_2]}{k_{7b}[O_2]+k_{7a}}$ from our experiments (performed at 294K and approximately 740-750 Torr) to that from Orlando et al. at 298K and 700 Torr. To calculate this fraction, we compare the production of ethylene glycol and glycolaldehyde. Recall that the following are the primary reactions that produce glycolaldehyde and ethylene glycol in our system:

$$\mathrm{RO}_2 + \mathrm{RO}_2 \to \mathrm{RO}^{\cdot} + \mathrm{RO}^{\cdot} + \mathrm{O}_2$$
 (4a)

$$\rightarrow \mathrm{RO^{\cdot}} + \mathrm{R_{-H}} {=} \mathrm{O} + \mathrm{HO}_2 \tag{4b}$$

$$\rightarrow \text{ROH} + \text{R}_{-\text{H}} = \text{O} + \text{O}_2 \tag{4c}$$

$$\rightarrow \text{ROOR} + \text{O}_2$$
 (4d)

$$\operatorname{HOCH}_{2}\operatorname{CH}_{2}\operatorname{O}^{\cdot} \xrightarrow{O_{2}} 2\operatorname{CH}_{2}\operatorname{O} + \operatorname{HO}_{2}^{\cdot}$$
 (7a)

$$\xrightarrow{O_2} \text{HOCH}_2\text{CHO} + \text{HO}_2^{\cdot} \tag{7b}$$

Therefore, the production rates of glycolaldehyde and ethylene glycol can be expressed as follows, where GA is glycolaldehyde and EG is ethylene glycol:

$$P_{GA} = k_{7b}[RO][O_2] + k_4[RO_2]^2(\alpha_{4c} + \alpha_{4b})$$
$$P_{EG} = k_4\alpha_{4c}[RO_2]^2$$

Solving for the steady state concentration of alkoxy radicals ([RO]), where γ is the fraction of thermalized alkoxy radicals in this system (we assume that the fraction of alkoxy radicals that are not stabilized do not form GA):

$$[RO] = \gamma \frac{k_4 \alpha_{4b} [RO_2]^2 + 2k_4 \alpha_{4a} [RO_2]^2}{k_{7b} [O_2] + k_{7a}}$$

Substituting this into the equation for the production of glycolaldehyde yields:

$$P_{GA} = k_{7b}\gamma[O_2]\left(\frac{k_4\alpha_{4b}[RO_2]^2 + 2k_4\alpha_{4a}[RO_2]^2}{k_{7b}[O_2] + k_{7a}}\right) + k_4[RO_2]^2(\alpha_{4c} + \alpha_{4b})$$

Finally, taking the ratio of P_{GA} to P_{EG} we obtain:

$$\frac{P_{GA}}{P_{EG}} = \gamma(\frac{\alpha_{4b} + 2\alpha_{4a}}{\alpha_{4c}})(\frac{k_{7b}[O_2]}{k_{7b}[O_2] + k_{7a}}) + \frac{\alpha_{4c} + \alpha_{4b}}{\alpha_{4c}}$$

Therefore, we can derive $\frac{k_{7b}[O_2]}{k_{7b}[O_2]+k_{7a}}$ from the ratio of [GA] to [EG] in our experiments. We determine the y-intercept of this equation by extrapolating our low $[O_2]$ experiments to $[O_2] = 0$, and obtain a value of $\frac{\alpha_{4c} + \alpha_{4b}}{\alpha_{4c}} = 1.3 \pm 0.3$. The value of $\frac{\alpha_{4b} + 2\alpha_{4a}}{\alpha_{4c}}$ is determined from the full fit of our box model to our data. The results of this fit (and therefore the resulting values of α_{4b} , α_{4a} , and α_{4c}) are not particularly sensitive to the value of $\frac{k_{7b}[O_2]}{k_{7b}[O_2]+k_{7a}}$. We obtain a value of $\frac{\alpha_{4b}+2\alpha_{4a}}{\alpha_{4c}} = 1.4$. The only remaining unknown is γ . We can estimate γ by comparing our data to that of Orlando et al,² and assuming that $\frac{k_{7b}[O_2]}{k_{7b}[O_2]+k_{7a}}$ is equal in both experiments, which yields $\gamma = 0.68$, slightly smaller than $\gamma = 0.74$ determined by Orlando et al. While this may encompass true differences in $\frac{k_{7b}[O_2]}{k_{7b}[O_2]+k_{7a}}$, the difference is well within the uncertainty in our estimate of the sensitivities of EG and GA. Our data is plotted alongside the data of Orlando et al in Figure S4, assuming $\gamma = 0.68$. Figure S4 also shows data from a similar experiments by Barnes et al,³ who likewise observe an excess of glycolaldehyde at a wide range of $[O_2]$. The low O_2 intercept observed by Barnes et al. varied from 1.4 to 1.6, somewhat higher than, but within the uncertainty of, our results. The intercept of Barnes at al. is pressure dependent and the difference between this intercept and our intercept has been subtracted from the Barnes data in Figure S9. The alkoxy radicals generated in their system were also generated from the RO_2 self-reaction and, at similar pressures, match our results quite closely across the range of $[O_2]$, when the Barnes data is adjusted to match our intercept at 994 hPa. Given the results shown in Figure S4, in our box model, we use a value of 20% for the branching to reaction with O_2 for the alkoxy reactions in air at 745 Torr and 294K, and assign the low O_2 intercept to a tentative additional reaction pathway of the self-reaction (Reaction 4b). In air, about half of the excess glycolaldehyde is attributed to this additional pathway, albeit with significant uncertainty.



Figure S4: Fraction of alkoxy radicals that proceed by reaction with O_2 , as determined from our data, the data of Barnes et al,³ and the data of Orlando et al.² The Orlando data is plotted assuming $\gamma = 0.68$ for the yield of thermalized alkoxy radicals at 994 hPa. The data of Barnes et al are adjusted to match our intercept at low $[O_2]$.

As the primary production of the ROOH relative to the production of glycolaldehyde increases (more HO₂ relative to RO₂), significant glycolaldehyde is produced secondarily via both ROOH photolysis and its reaction with 'OH. Over the range of HO₂ production for our experiments in air, the box model predicts that the ratio of glycolaldehyde to ethylene glycol will increase by approximately 50% as a result of this secondary production. As illustrated in Figure S5, the data are consistent with the predictions from the box model. Additionally, the data are consistent with a maximum 0.4% branching to the formation of glycolaldehyde, or a 2% branching to the formation of alkoxy radicals, via this chemistry. This therefore suggests the source of glycolaldehyde formation via the $RO_2^{\circ}+HO_2^{\circ}$ reaction is quite small. We therefore neglect this source in our analysis. Including this source in our analysis does not change our predicted value of α_{4d} , and changes our predicted value of k_4 by less than 5%.



Figure S5: The ratio between glycolaldehyde and ethylene glycol as a function of the ratio of simulated RO_2^{\cdot} to HO_2^{\cdot} steady state concentration, both as observed and as simulated in the photochemical box model. The red line is the box model run with no glycolaldehyde production via $RO_2^{\cdot} + HO_2^{\cdot}$ chemistry. The green line is the box model run with a branching fraction of .02 to the formation of RO' and 'OH via the $RO_2^{\cdot} + HO_2^{\cdot}$ reaction or, equivalently, a branching fraction of .004 to the direct formation of glycolaldehyde via the $RO_2^{\cdot} + HO_2^{\cdot}$ reaction.

4 Appendix D: Reactions, Rate Constants, and Photolysis Frequencies in the Photochemical Box Model

Table S4: Bimolecular and termolecular reactions and rate constants. $R = HOCH_2CH_2$. All rate constants are given at 294 K at 993 hPa of air. ^aRate constant used is that of 'OH + methyl hydroperoxide. ^bRate constant used is 50% that of the total reaction rate constant of 'OH + ethylene glycol. ^cConcentrations are in units of molecules cm⁻³. ^dTotal reaction rate constant for all reaction channels. ^eThis rate constant is not explicitly included in the box model, and is assumed to be arbitrarily fast.

Bimolecular Reaction	Rate Constant ^d	α	Source
	$(10^{-12} \frac{cm^3}{molec*s})$		
$CH_2 = CH_2 + OH \xrightarrow{O_2} HOCH_2CH_2O_2$	8.1	1	4
$\mathrm{CH}_{3}\mathrm{OH}+\mathrm{^{\cdot}OH}\xrightarrow{\mathrm{O}_{2}}\mathrm{HO}_{2}^{\cdot}+\mathrm{CH}_{2}\mathrm{O}+\mathrm{H}_{2}\mathrm{O}$.90	1	4
$\mathrm{RO}_2^{\boldsymbol{\cdot}} + \mathrm{HO}_2^{\boldsymbol{\cdot}} \to \mathrm{ROOH} + \mathrm{O}_2$	11	1	5
$\mathrm{RO}_2^{\boldsymbol{\cdot}} + \mathrm{RO}_2^{\boldsymbol{\cdot}} \to \mathrm{ROOR} + \mathrm{O}_2$	fitted (k_4)	fitted (α_4)	
$\rightarrow 2 RO' + O_2$		1 - 3.01 α_4	
\rightarrow HOCH ₂ CHO + ROH + O ₂		$1.75\alpha_4$	
\rightarrow RO' + HOCH ₂ CHO + HO ₂		$0.26 \alpha_4$	
$\operatorname{RO}^{\cdot} \xrightarrow{\operatorname{O}_2} \operatorname{HCHO} + \operatorname{HO\dot{C}H}_2$	е	0.8	this work
$\xrightarrow{O_2} HOCH_2CHO + HO'_2$		0.2	
$\rm HO\dot{C}H_2 + O_2 \rightarrow \rm HCHO + \rm HO_2^{\textbf{\cdot}}$	9.1	1	4
$^{\circ}\mathrm{OH} + \mathrm{ROH} \xrightarrow{\mathrm{O}_{2}} \mathrm{HOCH}_{2}\mathrm{CHO} + \mathrm{HO}_{2}^{\circ} + \mathrm{H}_{2}\mathrm{O}$	14.5	1	6
$^{\circ}\mathrm{OH} + \mathrm{HCHO} \xrightarrow{\mathrm{O}_2} \mathrm{HO}_2^{\circ} + \mathrm{CO} + \mathrm{H_2O}$	8.4	1	4
$^{\circ}\mathrm{OH} + \mathrm{HOCH_{2}CHO} \xrightarrow{\mathrm{O}_{2}} \mathrm{HO}_{2}^{\circ} + \mathrm{O} = \mathrm{CHCH} = \mathrm{O} + \mathrm{H_{2}O}$	11	.2	4
$\rightarrow \mathrm{HOCH}_2\mathrm{C}(\mathrm{O})\mathrm{O}_2^{\boldsymbol{\cdot}} + \mathrm{H}_2\mathrm{O}$.8	4
$^{\cdot}\mathrm{OH} + \mathrm{ROOH} \rightarrow \mathrm{RO}_{2}^{\cdot} + \mathrm{H}_{2}\mathrm{O}$	$3.6^{\mathbf{a}}$	1	
$\xrightarrow{O_2} CH(O)CH_2OOH + HO_2 + H_2O$	$7.2^{\mathbf{b}}$	1	
\rightarrow HOCH ₂ CHO + 'OH + H ₂ O	8.2 ^a	1	
$^{\cdot}\mathrm{OH} + \mathrm{H_2O_2} \rightarrow \mathrm{HO_2^{\cdot}} + \mathrm{H_2O}$	1.8	1	4
$\rm ^{\circ}OH + HO_{2}^{\circ} \rightarrow H_{2}O + O_{2}$	110	1	4
Termolecular Reaction	Rate Constant ^d	α	Source
	$(10^{-12} \ \frac{cm^6}{molec^2 * s})$		
$\mathrm{HO}_2^{\boldsymbol{\cdot}} + \mathrm{HO}_2^{\boldsymbol{\cdot}} \to \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2$	$1.4 + 1.18(1 + (2.5 \times 10^{-6})[\text{H}_2\text{O}])^{\mathbf{c}}$	1	4
$\mathrm{HO}_2^{\boldsymbol{\cdot}} + \mathrm{HO}_2 \boldsymbol{\cdot} \operatorname{CH}_3\mathrm{OH} \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2 + \mathrm{CH}_3\mathrm{OH}$	$(1.4{\times}10^{-17})[{\rm CH_{3}OH}]^{\bf c}$	1	7

Table S5: Photolysis Reactions. $R = HOCH_2CH_2$. ^aFor ROOH and ROOR, we use the measured photolysis rate over 120 s for H_2O_2 in the model, as we expect the photolysis rates of these compounds to be similar. We did measure an upper limit to the photolysis rates of these compounds, and these measurements are discussed in Appendix F.

Reaction	Photolysis Frequency (s^{-1})
$H_2O_2 \rightarrow OH + OH$	3.0×10^{-4}
$\mathrm{ROOH} \rightarrow \mathrm{RO^{*}} + \mathrm{^{*}OH}$	$3.0\times10^{-4}~{\rm a}$
$ROOR \rightarrow RO' + RO'$	$3.0 \times 10^{-4} \ \mathbf{a}$
$\rm HOCH_2CHO \rightarrow \rm HO\dot{C}H_2 + \rm HCO$	1.7×10^{-4}

Table S6: Decay in the dark following photolysis. $R = HOCH_2CH_2$

Compound	Measured decay rate (s^{-1})
ROOR	5.5×10^{-5}
ROOH	3.4×10^{-5}

5 Appendix E: Levenberg-Marquardt Optimization

	Table S	7: Least	Squares	Levenberg-N	Aarquardt C	Optimization	Parameters
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Constraint	Value
Step Size Factor for Finite Differences	1×10^{-3}
Function Tolerance	1×10^{-6}
Step Tolerance	1×10^{-6}

6 Appendix F: GC Conditions

Table S8: GC Conditions. ^aTemperature Ramp 1: 15° C/min (- 45° C $\rightarrow 10^{\circ}$ C), 3 °C/min (10° C $\rightarrow 75^{\circ}$ C), 10 °C/min (75° C $\rightarrow 130^{\circ}$ C). ^bTemperature Ramp 2: 15° C/min (-45° C $\rightarrow 10^{\circ}$ C), 2.5 °C/min (10° C $\rightarrow 45^{\circ}$ C), 1.5 °C/min (45° C $\rightarrow 60^{\circ}$ C), 10 °C/min (60° C $\rightarrow 130^{\circ}$ C). ^cThe GC No. indicates for which GCs of that experiment the listed conditions apply, where BG is the background GC (taken before the lights were turned on), 1 is the first GC after the lights were turned off, etc. ^dThe factor by which the sample of air is diluted with N₂ before being trapped onto the head of the column.

Experiment No. GC No. ^c Trap Temperature (°C)		Trap Time (min)	Temperature Ramp	Dilution Factor ^d	
6	6 BG, 1, 2, 3 -45		5	Ramp 1 ^a	4
7 BG -45		-45	5	Ramp 1	4
	1, 2	-45	10	Ramp 1	4
8	BG	-45	5	Ramp $2^{\mathbf{b}}$	4
	1	-45	10	Ramp 2	4
9	BG	-45	5	Ramp 2	4
	1, 2	-45	10	Ramp 2	4
10	BG	-45	5	Ramp 2	4
	1	-45	10	Ramp 2	4
11	BG	-45	7	Ramp 2	4
	1	-45	12.8	Ramp 2	4
	2	-45	10	Ramp 2	4
12	BG	-45	5	Ramp 2	4
	1	-45	10	Ramp 2	4
	2	-45	10	Ramp 1	4
13	BG	-45	5	Ramp 1	4
	1	-45	10	Ramp 1	4
	2	-45	10	Ramp 1	5
14	BG	-45	5	Ramp 1	4
	1,2	-45	10	Ramp 1	4
15	BG	-45	5	Ramp 1	4
	1,2	-45	10	Ramp 1	4
16	BG	-45	5	Ramp 1	4
	1	-45	10	Ramp 1	4
17	BG	-45	5	Ramp 1	4
	1	-45	5	Ramp 1	6
18	BG	-45	5	Ramp 1	4
	1	-45	5	Ramp 1	6
19	BG	-45	10	Ramp 1	6
	1	-45	3	Ramp 1	8
20	BG	-45	3	Ramp 1	4
	1	-45	5	Ramp 1	4
	2	-40	10	Ramp 1	6

7 Appendix G: Peroxide Synthesis and NMR Analysis

NMR Data. Spectral data for hydroxyhydroperoxide 1: ¹H NMR (400 MHz, CDCl₃) δ 4.16 – 4.13 (AA'XX' m, 2H), 3.92 – 3.90 (AA'XX' m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 78.0, 61.0; IR (thin film, NaCl) 3310, 2944, 1465, 1066, 1031.

Spectral data for ether **2**: ¹H NMR (400 MHz, CDCl₃) δ 4.18-4.16 (AA'XX' m, 2H), 3.80-3.76 (m, 4H), 3.66-3.64 (AA'XX' m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 75.6, 72.7, 68.7, 61.8; IR(thin film, NaCl) 3315, 2916, 1505, 1472, 1443, 1239, 1122, 1069.



Figure S6: ¹H NMR (400MHz, CDCl₃) of compound $\mathbf{1}$.



Figure S7: Infrared spectrum (Thin Film, NaCl) of compound **1**.



Figure S8: $^{13}\mathrm{C}$ NMR (100 MHz, CDCl_3) of compound 1.



Figure S9: ¹H NMR (400 MHz, CDCl₃) of compound $\mathbf{2}.$



Figure S10: Infrared spectrum (Thin Film, NaCl) of compound **2**.



Figure S11: 13 C NMR (100 MHz, CDCl₃) of compound **2**.

8 Appendix H: Table of Results

Experiment No.	Δ [Ethene] ^a	$\mathbf{F}_{external}^{\mathbf{b}}$	[ROOR]	[ROH]	[ROOH]	$[R_{\text{-H}}{=}O]$
1	91	.12	6.2	12.1	28.5	19.3
2	56	1.68	.86	1.8	50.2	3.5
3	19	.02	1.6	3.3	6	5.5
4	48	.05	4.4	7.9	15	12.4
5	46	.04	3.9	7.4	13.7	11.9
6	104	.14	7.7	13.6	38.5	21.1
7	81	.23	5.1	9.3	32.7	14.6
8	31	3.5	.13	.34	25.5	.90
9	107	.31	6.0	10.4	47.3	16.0
10	95	.46	5.2	9.2	56	14.6
11	68	.62	3.5	6.5	43	10.7
12	31	2.94	.29	.55	25.9	1.3
13	26	4.48	.14	.33	22.4	.88
14	31	.04	2.3	4.2	7.2	6.7
15	32	3.55	.19	.43	25.8	1.0
16	37	3.35	.28	.59	35.3	1.3
17	87	.10	7.2	12.2	25.9	18.9
18	49	.10	2.7	6.0	12.8	9.8
19	14	3.60	.18	.25	12.7	.70
20	7	3.48	.09	.20	8.4	.53

Table S9: Experimental Results. All concentrations are in ppbv. ${}^{\mathbf{a}}\Delta$ [Ethene] is determined by the box model. ${}^{\mathbf{b}}F_{external}$ is the ratio of HO₂ produced via methanol and H₂O₂ chemistry to the RO₂ produced via the reaction of ethene with 'OH.

A Note on the Results. An increasing background interference was observed in the ethylene glycol (m/z 147) signal as a function of time after the oxidation period, which most significantly affected the observed ethylene glycol concentrations during experiments with

low ethylene glycol production. This background interference was not observed in the GC data. The signal at m/z 149 closely tracked the non-ethylene glycol background signal at m/z 147. Therefore, we accounted for the non-ethylene glycol background by subtracting the signal at m/z 149 from the m/z 147 signal. Additionally, to increase the signal to noise ratio in the HRToF, the configuration of the instrument was changed in September 2022 to increase the amount of air entering the mass filter ion optics. This resulted in a small change of the observed ratio of glycolaldehyde to ethylene glycol in this study for identical experiments (+10%). As the most careful effort to characterize the CIMS sensitivities to EG and GA occurred after the gas load was increased, we placed the data for all the experiments on a common footing by multiplying the GA concentrations by 1.10 for the data obtained prior to September 2022. We confirmed this correction by replicating an ethylene glycol oxidation experiment and comparing the resulting observed m/z 145 signals before and after the configuration change. Illustrating how sensitive our estimate of α_{4b} is to small changes in the relative sensitivity of GA to ethylene glycol, the 10% increase in GA increased α_{4b} by 50%. The stated uncertainty in α_{4b} is increased to account for this additional source of potential error. Our estimate of the total fraction of radical propagating channels remains the same, as well as our estimate of α_{4c} and α_{4d} . α_{4b} is particularly sensitive to this correction, while other branching fractions are not, due to the method of determining this branching fraction - while other branching fractions are determined from ratios of concentrations, α_{4b} is determined by the difference of two ratios, therefore greatly increasing its uncertainty.

9 Appendix I: Mass Balance in Oxidation Experiments

Figure S12 shows the ratio between the carbon measured in the products and the reacted ethene (predicted by our box model) in our ethene oxidation experiments. The carbon of the measured products is determined by noting that two peroxy radicals are consumed for each ROOR formed, and 2 peroxy radicals are reacted for each ethylene glycol formed. The sum of these should then account for approximately 66% of the carbon produced in the self-reaction. Additionally, one peroxy radical is consumed for each ROOH formed. Figure S12 demonstrates that our measured products match the reacted ethene quite closely across the range of $F_{external}$.



Figure S12: The ratio between ethene-derived products and Δ [Ethene] as a function of $F_{external}$, where $F_{external}$ is the ratio of HO₂ produced via methanol and H₂O₂ chemistry to the RO₂ produced via the reaction of ethene with 'OH. Points in blue are experiments performed without butanediol, and points in red are experiments performed with butanediol. Square points include only the carbon from the RO₂ self-reaction in the numerator, while the circle points include the products of the RO₂ + HO₂ reaction. The solid green line is the line indicating a 1:1 relationship between the measured products and reacted ethene, and the two dashed lines enclose the points within ±25% of mass balance.

10 Appendix J: Calculated Polarizabilities and Dipole Moments

The dipole moment and polarizability are calculated at the B3LYP/cc-pVTZ level. The dipole moment is reported below as the weighted averages of the low energy conformers, and the polarizabilities are those of the lowerst-energy conformer.⁸ Using these dipole moment and polarizability estimates, ion-molecule collision rate coefficients ($k_{cap}(T)$) are calculated using the parameterization of Su et al⁹ (Equations 3 - 6), where q is the charge of the electron, α is the polarizability of the molecule, μ_D is the dipole moment, μ is the reduced mass of the molecule and the ion, k_B is the Boltzmann constant, and T is the temperature.

$$k_L = 2\pi q \sqrt{\frac{\alpha}{\mu}} \tag{3}$$

$$x = \frac{\mu_D}{\sqrt{2\alpha k_B T}} \tag{4}$$

$$K_{cap} = \begin{cases} 0.4767x + 0.6200 & x \ge 2\\ \frac{(x+0.5090)^2}{10.526} + 0.9754 & x \le 2 \end{cases}$$
(5)

$$k_{cap}(T) = K_{cap} \times k_L \tag{6}$$

11 Appendix K: Calculation of Uncertainties

11.1 Sensitivities

For the measured sensitivities, the uncertainty is calculated as a standard deviation of replicate measurements. In the case of 2,3-butanediol, where only one measurement was taken, the error in the sensitivity is calculated by propagating the error from the measured weight of the compound and the uncertainty in the CIMS signal. Similarly, the error in 2-hydroxy-

Compound	α (Å ³) μ_D (D)		Collision Rate Coefficient	
			$(10^{-9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})$	
Ethylene glycol	5.11	2.08	1.91	
H_2O_2	1.78	1.77	1.78	
2,3-butanediol	8.6	2.2	1.94	
2-hydroxy-3-butanone	8.10	3.09	2.46	
Glycolaldehyde	4.64	2.33	2.06	
HOCH ₂ CH ₂ OOCH ₂ CH ₂ OH	10.16	2.45	2.01	
HOCH ₂ CH ₂ OOH	5.91	2.44	2.05	
Diethylene Glycol	9.34	2.17	1.88	

Table S10: Calculated Polarizabilities, Dipole Moments, and $\rm CF_3O^--Molecule$ Collision Rate Coefficients for Compounds of Interest. T = 298K

3-butanone was determined by propagating the error in the CIMS signal and the error in the 2,3-butanediol concentration. The error of the calculated sensitivities was determined by propagating the error of the ethylene glycol sensitivity, from which they were calculated.

11.2 Photolysis Rates

Uncertainties in the photolysis rates of ROOH and ROOR are derived from the standard deviation of the two measurements. Uncertainties in the photolysis frequencies of H_2O_2 and glycolaldehyde are determined by the uncertainty in the fitted slopes used to determine these photolysis frequencies.

11.3 Self-Reaction Parameters

The error in the self-reaction parameters is calculated by propagating the errors from the various error sources, as listed in the main body of the paper. The error of each of these constraints was determined as follows.

- 1. Q: Determined by propagating the errors in the post-oxidation CIMS signals and the errors in the sensitivities of each of the compounds. The error in the CIMS signals was determined to be the standard deviation of the signal during the equilibration period.
- 2. $\mathbf{F}_{external}$: Determined by propagating the errors in the ethene, methanol, and H₂O₂ concentrations, which each have errors of 10%, and the rate constants of each of their reactions with 'OH, which each have errors of 15%.
- 3. Fit: Determined using a bootstrapping method.
- 4. Ratios of Sensitivities: Determined by propagating the errors of the individual sensitivities, which are calculated as described above.

References

- Lee, R.; Gryn'ova, G.; Ingold, K. U.; Coote, M. L. Why are sec-alkylperoxyl bimolecular self-reactions orders of magnitude faster than the analogous reactions of tertalkylperoxyls? The unanticipated role of CH hydrogen bond donation. *Physical Chemistry Chemical Physics* **2016**, *18*, 23673–23679.
- (2) Orlando, J. J.; Tyndall, G. S.; Bilde, M.; Ferronato, C.; Wallington, T. J.; Vereecken, L.; Peeters, J. Laboratory and Theoretical Study of the Oxy Radicals in the OH- and Cl-Initiated Oxidation of Ethene. *The Journal of Physical Chemistry A* 1998, 102, 8116– 8123.
- (3) Barnes, I.; Becker, K. H.; Ruppert, L. FTIR product study of the self-reaction of hydroxyethl peroxy radicals. *Chemical Physics Letters* **1993**, 203, 295–301.
- (4) Burkholder, J. B.; Sander, S.; Abbatt, J.; Barker, J. R.; Cappa, C.; Crounse, J. D.;
 Dibble, T. S.; Huie, R. E.; Kolb, C. E.; Kurylo, M. J.; Orkin, V. L.; Percival, C. J.;
 Wilmouth, D. M.; Wine, P. H. Chemical Kinetics and Photochemical Data for Use in

Atmospheric Studies, Evaluation No. 19. JPL Publication 19-5, Jet Propulsion Laboratory, Pasadena, 2019 http://jpldataeval.jpl.nasa.gov.

- (5) Wennberg, P. O.; Bates, K. H.; Crounse, J. D.; Dodson, L. G.; McVay, R. C.; Mertens, L. A.; Nguyen, T. B.; Praske, E.; Schwantes, R. H.; Smarte, M. D.; St Clair, J. M.; Teng, A. P.; Zhang, X.; Seinfeld, J. H. Gas-Phase Reactions of Isoprene and Its Major Oxidation Products. *Chemical Reviews* **2018**, *118*, 3337–3390, Publisher: American Chemical Society.
- (6) Mellouki, A.; Ammann, M.; Cox, R. A.; Crowley, J. N.; Herrmann, H.; Jenkin, M. E.; McNeill, V. F.; Troe, J.; Wallington, T. J. Evaluated kinetic and photochemical data for atmospheric chemistry: volume VIII – gas-phase reactions of organic species with four, or more, carbon atoms (≥ C₄). Atmospheric Chemistry and Physics **2021**, 21, 4797–4808, Publisher: Copernicus GmbH.
- (7) Christensen, L. E.; Okumura, M.; Hansen, J. C.; Sander, S. P.; Francisco, J. S. Experimental and ab Initio Study of the HO2·CH3OH Complex: Thermodynamics and Kinetics of Formation. *The Journal of Physical Chemistry A* 2006, *110*, 6948–6959.
- (8) Garden, A. L.; Paulot, F.; Crounse, J. D.; Maxwell-Cameron, I. J.; Wennberg, P. O.; Kjaergaard, H. G. Calculation of conformationally weighted dipole moments useful in ion-molecule collision rate estimates. *Chemical Physics Letters* **2009**, *474*, 45–50.
- (9) Su, T.; Chesnavich, W. J. Parametrization of the ion-polar molecule collision rate constant by trajectory calculations. *The Journal of Chemical Physics* **1982**, *76*, 5183–5185.